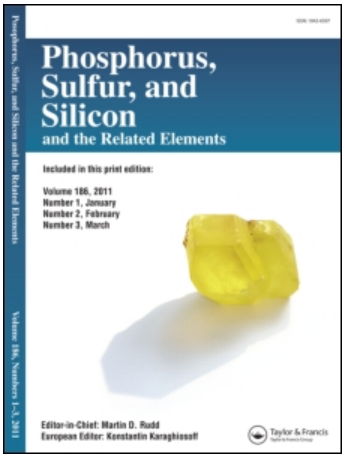

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Zhou, Yuehui and Hartmann, Horst(1996) 'ON THE REACTION OF ω-SELENOCYANATOACETOPHENONES WITH ALIPHATIC AMINES—FORMATION OF AROYL SELENOAMIDES', Phosphorus, Sulfur, and Silicon and the Related Elements, 118: 1, 293 — 299
To link to this Article: DOI: 10.1080/10426509608038820
URL: http://dx.doi.org/10.1080/10426509608038820

Phosphorus, Sulfur, and Silicon, 1996, Vol. 118, pp. 293–299
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Communication

ON THE REACTION OF ω-SELENOCYANATOACETOPHENONES WITH ALIPHATIC AMINES—FORMATION OF AROYL SELENOAMIDES

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(Received 17 June 1996)

By the reaction of ω-selenocyanatoacetophenones **2** with aliphatic secondary amines instead of 2-amino-4-aryl-selenazoles **7** aroyl selenoamides **11** are formed. Some of the spectroscopic data of the new selenoamides **11** are recorded, and the mechanism of their formation is discussed.

Keywords: ω-selenocyanatoacetophenones; aroyl selenoamides; willgerodt-kindler type reaction; 2-dialkylamino-selenazoles

INTRODUCTION

ω-Thiocyanato-acetophenones **1** are versatile synthons in organic chemistry. They can be prepared very easily by the reaction of corresponding ω-bromoacetophenones with alkali or ammonium thiocyanates [1] and transformed into different types of products, especially heterocyclic compounds [2]. E.g. the thiocyanatoacetophenones **1** can react, via the intermediates **4**, with several nucleophilic reagents of the general structure HY (**3**) to give sulphur-containing heterocycles of the general structure **6** [3] or **8** [4]. The 2-amino-thiazoles **6** (Y = NR_2) which are formed if Y in **3** is a secondary amino moiety are of large interest because they can be used as educts for preparing different

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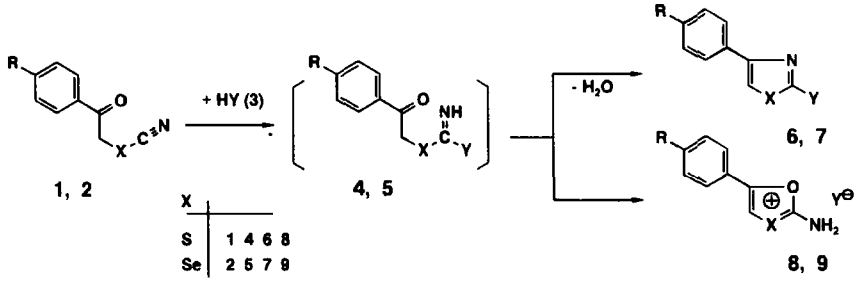
types of organic dyes, such as 2-amino-thiazolyl substituted azo dyes [5], methine dyes [6], or squaraines [7].



SCHEME 1.

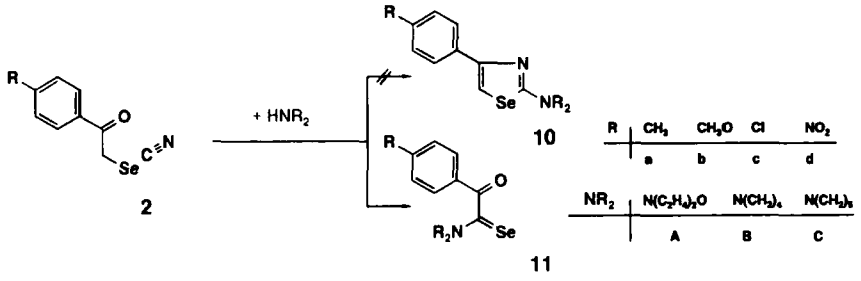
It should be expected that ω-selenocyanatoacetophenones of the general structure **2** which are seleno analogues of the ω-thiocyanatoacetophenones **1** and available analogously to them by reaction of corresponding ω-bromoacetophenones with alkali selenocyanides [8] react similar with the same type of nucleophilic compounds **3** to give the seleno heterocycles **7** and **9**. Indeed, the ω-selenocyanatoacetophenones **2** can be transformed into the 1,3-oxaselenolium salts **9** if they are allowed to react with strong mineralic acid at lower temperature [9].

Surprisingly, there are no works in the literature until now to transform the ω-selenocyanatoacetophenones **2** into corresponding 2-amino-selenazoles **7** ($Y = NR_2$) by their reaction with ammonia or primary or secondary amines [10].

RESULTS

By performing this transformation reaction with secondary aliphatic amines under similar conditions which have been applied for the preparation of N(2)-disubstituted 2-aminothiazoles **6** ($Y = NR_2$) [3] we found, however, that the expected 2-amino-selenazoles **7** ($Y = NR_2$) are formed in very low yields only. Instead of them, non-heterocyclic aroyl selenoamides of the general structure **11** are formed.

These compounds **11** could be obtained in satisfactory yields by adding an equimolar amount of a secondary aliphatic amine into an ethanolic solution of a ω-selenocyanatoacetophenone **2** and heating the resulting mixture for few minutes at reflux temperature. After cooling the aroyl selenoamides **11** so formed crystallize from the reaction mixture and could be isolated by suction. The 2-dialkylamino-selenazoles **10** simultaneously formed in some extent could be



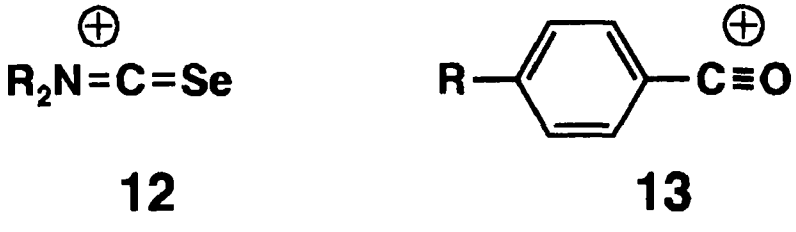
SCHEME 2.

detected, in few examples, in the filtrate by their coupling reaction with appropriate aryl diazonium salts only. In Table I the aroyl selenoamides **11** prepared are listed.

The ω-selenocyanatoacetophenone educts **2** necessary for this transformation have been prepared from corresponding ω-bromoacetophenones by their reaction with alkali selenocyanides in acetone accordingly to a method reported in the literature [8]. Some of their characteristic analytical and spectral data are summarised in Table II.

DISCUSSION

The nearly unknown [11] aroyl selenoamides **11** are yellow to orange coloured crystalline compounds their analytical and spectroscopic data (see Table III) are in accordance with their given structure. E.g. the aroyl selenoamides **11** exhibit in their mass spectra, besides a typical mol peak, two characteristic peaks which can be attributed to both the fragment ions **12** and **13** formed in course of a C-C bond scission. Furthermore, the selenium isotope pattern in the corresponding mol peaks and in the fragment ions **13** is clearly recognised.



SCHEME 3.

TABLE II Characteristical data of the ω-selenocyanatoacetophenone educts **2**

Nr	*R*	*yield [%]*	*m.p. [°C] (Lit.)*	*Formula (M.w.)*		*C*	*H*	*N*	*Cl*
2a	CH_3	52	131–133	$C_{10}H_9NOSe$	calcd.	50.42	3.78	5.88	
				(238.0)	found	50.19	3.70	5.73	
2b	CH_3O	95	118–119	$C_{10}H_9NO_2Se$	calcd.	47.24	3.54	5.35	
				(254.0)	found	47.03	3.25	5.35	
2c	Cl	73	140–143	$C_9H_6ClNOSe$	calcd.	41.78	2.32	5.42	13.73
				(258.5)	found	41.72	2.22	5.47	13.83
2d	NO_2	75	124–125	$C_9H_6N_2O_3Se$	calcd.	48.21	3.13	6.23	
			(123.5 [8b])	(269.0)	found	48.36	2.99	6.22	

In their ^{13}C NMR spectra the aroyl selenoamides **11** exhibit characteristic signals at about 185 and 200 ppm which can be attributed to their carbonyl and seleno carbonyl moieties resp., unambiguously. On the other hand, the aroyl selenoamides **11** do not exhibit in their ^1HNMR spectra any signals which should be attributed to a proton at C-5 of a 2-amino-selenazole moiety.

In their UV/VIS spectra the aroyl selenoamides **11** prepared exhibit long-wavelength absorptions with maxima at about 300 nm and longer-wavelength shoulders which can be attributed to n-π* transitions localised at the C═Se group [12].

The unexpected formation of the new N,N-disubstituted aroyl selenoamides **11** can be explained by assuming that the secondary amine used as reagent react primary with the ω-selenocyanatoacetophenone educts **2**, not at the CN triple

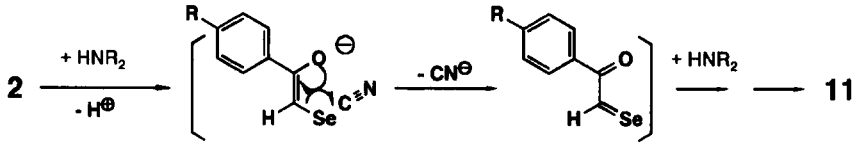
TABLE I Characteristical data of the aroyl selenoamides **11** synthesised

Nr	*NR_2*	*R*	*yield [%]*	*m.p. [°C]*	*Formula (M.w.)*		*C*	*H*	*N*	*Cl*
11Aa	$N(C_2H_4)_2O$	CH_3	30	133–134	$C_{13}H_{15}NO_2Se$	calcd.	52.70	5.07	4.73	
					(296.0)	found	52.90	5.54	4.35	
11Ab	$N(C_2H_4)_2O$	CH_3O	42	171–173	$C_{13}H_{15}NO_3Se$	calcd.	50.00	4.81	449	
					(312.0)	found	50.04	4.98	4.79	
11Ac	$N(C_2H_4)_2O$	Cl	35	169–170	$C_{12}H_{12}ClNO_2Se$	calcd.	45.49	3.79	4.42	11.22
					(316.5)	found	45.24	3.72	4.20	11.18
11Ad	$N(C_2H_4)_2O$	NO_2	46	192–193	$C_{12}H_{12}N_2O_4Se$	calcd.	44.04	3.67	8.56	
					(327.0)	found	43.95	3.63	8.45	
11Ba	$N(CH_2)_4$	CH_3	33	124–125	$C_{13}H_{15}NOSe$	calcd.	57.71	5.36	5.00	
					(280.0)	found	57.87	5.30	5.43	
11Bc	$N(CH_2)_4$	Cl	46	146–147	$C_{12}H_{12}ClNOSe$	calcd.	47.92	3.99	4.66	11.81
					(300.5)	found	47.98	4.15	4.72	11.68
11Bd	$N(CH_2)_4$	NO_2	25	172–174	$C_{12}H_{12}N_2O_3Se$	calcd.	46.30	3.86	9.00	
					(311.0)	found	46.60	3.37	8.53	
11Cc	$N(CH_2)_5$	Cl	30	112–113	$C_{13}H_{14}ClNOSe$	calcd.	49.60	4.45	4.45	11.29
					(314.5)	found	49.64	4.62	4.52	11.55

TABLE III Analytical data of the aroyl selenoamides **11** prepared

	MS [M/z]	*^{1}H-NMR, in $CDCl_3$ [δ-values]*	*^{13}C-NMR, in $CDCl_3$ [δ-values]*	λ_{max} [(log
Aa	297 $(MH)^+$, 239, 178 (**13**), 119 (**12**), 91	2.39 (s, 3H, CH_3), 3.54 (t, 2H, CH_2), 3.66 (t, 2H, CH_2), 3.92 (t, 2H, CH_2) 4.41 (t, 2H, CH_2), 7.26 (d, 2H, CH_{aryl}), 7.89 (d, 2H, CH_{aryl})	21.81 (CH_3), 50.84 (CH_2), 53.56 (CH_2), 66.25 (CH_2), 66.30 (CH_2), 129.58 (CH) 129.81 (CH), 130.74 (CC═O), 145.50 (CH), 188.89 (C═O), 201.39 (C═Se)	263 (4.1 298 (4.1 345 sh 393 sh
Ab	313 $(MH)^+$, 246, 135 (**12**), 91 65	3.54 (s, 2H, CH_2), 3.66 (s, 2H, CH_2), 3.85 (s, 3H, OCH_3), 3.90 (t, 2H, CH_2), 4.40 (t, 2H, CH_2), 6.93 (d, 2H, C_{haryl}), 7.97 (d, 2H, CH_{aryl}),	50.78 (CH_2), 53.43 (CH_2), 55.53 (OCH_3), 66.15 (CH_2), 114.12 (CH), 124.82 (CC═O), 132.02 (CH), 164.36 (CO), 188.18 (C═O), 201.21 (C═Se)	287 (4.3 297 (4.3 345 sh 380 sh
	316 $(MH)^+$, 258, 178 (**13**), 139 (**12**), 111, 39	3.54 (d, 2H, CH_2), 3.67 (d, 2H, CH_2), 3.91 (t, 2H, CH_2), 4.39 (t, 2H, CH_2), 7.43 (d, 2H, CH_{aryl}), 7.94 (d, 2H, CHaryl)	50.75 (CH_2), 53.56 (CH_2), 66.08 (CH_2), 66.11 (CH_2), 129.08 (CH), 130.86 (CH), 131.57 (CC═O), 140.55 (CCl), 187.19 (C═O), 199.90 (C═Se)	260 (4.2 299 (4.1 348 sh 400 sh
Ad	328 $(MH)^+$, 270, 178 (**13**), 150 (**12**), 134, 104, 86, 76, 59,	3.64 (m, 4H, CH_2), 4.34 (t, 2H, CH_2), 4.92 (t, 2H, CH_2), 8.19 (d, 2H, CH_{aryl}), 8.35 (d, 2H, CH_{aryl})	51.00 (CH_2), 54.02 (CH_2), 65.63 (CH_2), 124.15 (CH), 130.74 (CH), 138.23 (CC═O), 150.42 (CN), 185.35 (C═O), 196.85 (C═Se)	268 (4.2 309 (4.1 380 (3.4 434 (3.2
Ac	281 $(MH)^+$, 162 (**13**), 119 (**12**), 91, 70, 58, 43	2.01 (m, 4H, CH_2), 2.34 (s, 3H, CH_3), 3.31 (d, 2H, CH_2), 3.84 (d, 2H, CH_2), 7.20 (d, 2H, CH_{aryl}), 7.84 (d, 2H, CH_{aryl})	21.56 (CH_3), 23.58 (CH_2), 26.01 (CH_2), 52.31 (CH_2), 54.14 (CH_2), 129.23 (CH), 129.86 (CC═O), 144.99 (CCH_3), 189.53 (C═O), 196.35 (C═Se)	251 (4.0 297 (4.1 342 sh 395 sh
	301 $(MH)^+$, 162 (**13**), 149, 139 (**12**), 120, 111, 70, 55, 43,	2.09 (m, 4H; CH_2), 3.36 (t, 2H, CH_2), 3.88 (t, 2H, CH_2), 7.41 (d, 2H, CH_{aryl}), 7.95 (d, 2H, CH_{aryl}),	23.65 (CH_2), 26.12 (CH_2), 52.48 (CH_2), 128.91 (CH), 131.14 (CH), 131.60 (CC═O), 140.30 (CCl), 188.15 (C═O), 195.34 (C═Se)	271 (4.0 293 (4.1 352 sh 406 sh
Bd	312 $(MH)^+$, 162 (**13**), 150 (**12**) 120, 97, 70, 58, 43	2.13 (s, 4H, CH_2), 3.40 (t, 2H, CH_2), 3.89 (t, 2H, CH_2), 8.17 (d, 2H, CH_{aryl}), 8.25 (d, 2H, CH_{aryl}),	23.73 (CH_2), 26.23 (CH_2), 52.74 (CH_2), 54.52 (CH_2), 123.68 (CH), 130.86 (CH), 138.12 (CC═O), 150.38 (CN), 186.31 (C═O), 194.37 (C═Se)	273 (4.1 306 (4.1 380 sh 444 sh
Cc	314 $(MH)^+$, 176 (**13**), 139 (**12**) 112, 84, 69	1.61 (m, 2H, CH_2), 1.78 (q, 2H, CH_2), 1.86 (q, 2H, CH_2), 3.49 (t, 2H, CH_2), 4.32 (t, 2H, CH_2), 7.42 (d, 2H, CH), 7.95 (d, 2H, CH),	23.64 (CH_2), 25.25 (CH_2), 26.23 (CH_2), 51.91 (CH_2), 54.57 (CH_2), 129.00 (CH), 130.86 (CH), 131.72 (CC═O), 140,28 (CCl) 187.14 (C═O), 198.13 (C═Se)	254 (4.3 298 (4.2 353 sh 410 sh

bond of the selenocyanato group, but at their methylene groups under deprotonation to give rise, in a first step, to anionic species of the structure **14**. These anionic species can be transformed, by elimination of cyanide ions, into intermediate seleno aldehydes **15** which react, subsequently, with the starting amine HNR_2 to give the aroyl selenoamides **11** in a mechanistic pathway comparable with the one of the Willgerodt-Kindler reaction [13].



SCHEME 4.

The formation of intermediate seleno aldehydes **15** from ω-selenocyanatoacetophenones is also supposed by other authors to explain the formation of 2-aryl-substituted 1,3-selenoles from desyl selenocyanates by their reaction with an excess of sodium hydride in dimethoxyethane [14] or the formation of 3,6-dihydro-2H-selenopyranes from acceptor substituted alkyl selenocyanates by their reaction with 1,3-dienes in presence of a base, like triethylamine or lithium alkyls [15].

EXPERIMENTAL

Preparation of the ω-Selenocyanatoacetophenones 2 (General Procedure)

To a mixture of 7.2 g (0.05 mol) potassium selenocyanate in 100 ml acetone 0.05 mol of an appropriate ω-bromoacetophenone solved in some acetone was added dropwise at room temperature. After stirring for ten minutes, the resulting mixture is refluxed for 30 min and then cooled and diluted with water. The ω-selenocyanatoacetophenones formed crystallize and can be isolated by suction.

Preparation of N,N-Disubstituted Aroyl Selenoamides 11 (General Procedure)

To a solution of 0.05 mol of a ω-selenocyanatoacetophenone **2** in 100 ml ethanol 0.05 mol of a secondary aliphatic amine **10** are added under stirring at room temperature. After refluxing for 5 minutes the mixture is cooled, and the product crystallized is separated by suction.

Acknowledgements

The financial support of this work by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

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